Designation: D7365 – 09a (Reapproved 2022)

Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide[1]

This standard is issued under the fixed designation D7365; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice is applicable for the collection and preservation of water samples for the analysis of cyanide. This practice addresses the mitigation of known interferences prior to the analysis of cyanide. Responsibilities of field sampling personnel and the laboratory are indicated.

1.2 The sampling, preservation and mitigation of interference procedures described in this practice are recommended for the analysis of total cyanide, available cyanide, weak acid dissociable cyanide, and free cyanide by Test Methods D2036, D4282, D4374, D6888, D6994, D7237, D7284, and D7511. The information supplied in this practice can also be applied to other analytical methods for cyanide, for example, EPA Method 335.4.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2036 Test Methods for Cyanides in Water
D3370 Practices for Sampling Water from Flowing Process Streams
D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4282 Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion
D4374 Test Methods for Cyanides in Water—Automated Methods for Total Cyanide, Weak Acid Dissociable Cyanide, and Thiocyanate (Withdrawn 2012)[3]
D4411 Guide for Sampling Fluvial Sediment in Motion
D4840 Guide for Sample Chain-of-Custody Procedures
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6888 Test Method for Available Cyanides with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
D6994 Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection
D6696 Guide for Understanding Cyanide Species
D7237 Test Method for Free Cyanide and Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
D7284 Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas

[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

Diffusion Separation and Amperometric Detection
D7511 Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection

2.2 *U.S. EPA Methods:*[4]
EPA Method OIA-1677 Available Cyanide by Flow Injection with Ligand Exchange
EPA Method 335.2 Cyanide, Total (Titrimetric; Spectrophotometric)
EPA Method 335.4 Determination of Total Cyanide by Semi-Automated Colorimetry

2.3 *USGS Methods:*[5]
USGS I-3300-85
USGS I-4302-85

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129 and Guide D6696.

3.1.2 *refrigeration, n*—storing the sample between its freezing point and 6 °C.

3.1.3 *holding time, n*—the time lapsed from sample collection to sample analysis.

4. Summary of Practice

4.1 Samples are collected in appropriate containers and mitigated for known interferences either in the field during sample collection or in the laboratory prior to analysis.

5. Significance and Use

5.1 Cyanide is routinely analyzed in water samples, often to demonstrate regulatory compliance; however, improper sample collection or pretreatment can result in significant positive or negative bias potentially resulting in unnecessary permit violations or undetected cyanide releases into the environment.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in this practice. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water that meets the purity specifications of Type I or Type II water, presented in Specification D1193.

6.3 *Acetate Buffer*—Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2{\cdot}3H_2O$) in 500 mL of water. Add glacial acetic acid to yield a solution pH of 4.5, approximately 500 mL.

6.4 *Lead Acetate Test Strips*—Turns black in presence of sulfides. Moisten the paper with acetate buffer prior to use. Lead acetate test strips have been shown to be sensitive to about 50 mg/L S^{2-}.

6.5 *Potassium Iodide (KI) Starch Test Paper*—Turns blue in presence of free chlorine. Commercial alternative test strips may be used if they are shown to be at least as sensitive as the KI starch test strips.

6.6 *pH Indicator Test Strips*—pH indicator test strips capable of changing color at 0.5 pH units in the range of pH 2 to 12. More than one test strip may be necessary to cover this range.

6.7 *Sodium Hydroxide Solution (1 M)*—In a 1 L volumetric flask, dissolve 40 g NaOH in reagent water and dilute to volume.

6.8 *Sodium Hydroxide Solution (50 % wt/vol)*—In a beaker, dissolve 50 g NaOH in reagent water not to exceed 100 mL total volume, then transfer to a 100 mL volumetric flask and dilute to volume. (**Warning—**This is an exothermic reaction and the solution will become very hot while being prepared. It is recommended to place the solution in a water bath to cool.)

6.9 *Hydrated Lime*—$Ca(OH)_2$ powder.

6.10 *Ethylenediamine Solution (EDA), 3.5%*—Dilute 3.5 mL (or 3.15 g) of anhydrous $NH_2\ CH_2NH_2$ to 100 mL with water.

6.11 *Reducing Agents*—Ascorbic acid, sodium arsenite ($NaAsO_2$).

6.12 *Filter Paper or Syringe equipped with Leur-Lock Filters*—5 µm and 0.45 µm pore size. If unspecified, use 0.45 µm pore size.

6.13 *Dilute Acetic Acid*—Add 1 part glacial acetic acid to 9 parts water.

6.14 *Lead Carbonate ($PbCO_3$) or Lead Acetate ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$,* Lead acetate can be put in solution with water at a suggested concentration of 50 g/L.

6.15 *Sulfamic acid (0.4N), H_2NSO_3H*—Dissolve 40 g H_2NSO_3H in 1 L of water.

6.16 *Sample Bottles*—See 8.2 for further information about sample bottles.

7. Hazards

7.1 **Warning—**Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). Adequate ventilation is necessary when handling cyanide solutions and a fume hood should be utilized whenever possible.

[4] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

[5] Available from United States Geological Survey (USGS), USGS National Center, John W. Powell Bldg, 12201 Sunrise Valley Dr., Reston, VA 20192, http://www.usgs.gov.

[6] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.2 **Warning—**Many of the reagents used in these test methods are highly toxic. These reagents and their solutions must be disposed of properly.

8. Procedure

8.1 Laboratory personnel and field samplers should follow the practices described in Guide D3856. When sampling closed conduits such as process streams refer to Practices D3370. When sampling fluvial sediment in motion or open channel flow refer to Guide D4411. It is recommended to consult with the analytical laboratory prior to collecting samples to ensure the proper sample volume, containers, etc., as these parameters may vary depending on the analytical methods used to measure the cyanide.

8.2 *Sample Containers:*

8.2.1 Sample containers shall be made of materials that will not contaminate the sample, cleaned thoroughly to remove all extraneous surface contamination prior to use. Chemically resistant glass containers as well as rigid plastic containers made of high density polyethylene (HDPE) are suitable. Samples should be collected and stored in amber bottles to minimize exposure to ultraviolet radiation in the sample containers. If samples will only be tested for total cyanide, amber containers are not mandatory.

8.2.2 Virgin commercially-cleaned containers certified to be free of contamination are recommended; otherwise, wash containers with soap or biodegradable detergent if required, then dry by draining. For further information on sample containers, see Practices D3694.

8.3 *Sample Collection, Preservation, and Mitigation of Interferences:*

8.3.1 Collect a sample volume that is sufficient to the analytical method into a sample bottle described above. If the required sample volume is not specified, usually 1 L is sufficient for most analytical test methods, however, flow injection and automated methods usually consume considerably less sample volume than manual methods.

8.3.2 Unless otherwise specified, samples must be analyzed within 14 days. Certain sample matrices may require a shorter holding time or immediate analysis to avoid cyanide degradation due to interferences. Hold the sample no longer than the time necessary to preclude a change in cyanide concentration. A holding time study described in Practice D4841 is required if there is evidence that a change in cyanide occurs from interferences which would cause the holding time to be shorter than specified in this section, or within the time the sample would be held if shorter than the time specified in this section. Potential interferences and their corresponding analytical methods are shown in Table 1.

NOTE 1—It is recommended to investigate holding times for samples that meet any of the following conditions—disinfected by chloramination or ultraviolet irradiation, ammonia present and chlorinated, sulfur dioxide or sulfite used to dechlorinate, or if aldehydes are known or suspected to be present.

8.3.3 In the absence of interference, simple cyanides such as HCN, KCN, and NaCN are determined readily by each of the determinative steps, however, to determine "total" cyanide, metal cyanide bonds must be broken and cyanide separated to produce simple cyanide. In most total cyanide methods, this is accomplished by distillation from acid solution. Although distillation is assumed to eliminate or at least minimize most interferences, the high temperature and strong acid solutions can potentially introduce significant positive or negative bias. Interferences for total cyanide by distillation are listed in Tables 2 and 3. Interferences are also dependent on the determinative step, which are shown in Table 4.

8.3.4 There may be interferences that are not mitigated by this procedure. Any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method. Any removal or suppression technique not described in this practice or the analytical test method should be documented along with supporting data. A challenge solution with potential interferences for cyanide analysis is described in X1.1.1, which can be used as a sample matrix to examine analytical method performance.

8.3.5 Treat the sample immediately upon sample collection using any or all of the following techniques as necessary, followed by adjustment of the sample to pH > 10 and refrigeration. If applicable, laboratory mitigation techniques are also specified. Preserve the sample immediately (within 15 minutes of collection or treatment using procedures described in this practice) by adding 1 mL of 1M NaOH (6.7) per litre of sample, and then verify that the pH is greater than pH 10 with indicator test strips (6.6). If necessary, continue to add sodium hydroxide (6.7 or 6.8) drop wise until the pH is greater than pH 10 being careful not to add excess. Do not add NaOH if the cyanide concentration would change as a result of the addition.

8.3.5.1 Adding NaOH to samples containing formaldehyde (see Note 2 in 8.3.8) can possibly increase the cyanide concentration during storage. Conversely, adding NaOH to samples containing sulfite (see Note 3 in 8.4.2.2) can rapidly decrease the cyanide concentration. If the addition or lack of addition of NaOH would affect the holding time, hold the sample for a time no longer than the time necessary to maintain sample integrity (8.3.2).

8.3.6 *Sulfide*—During sample collection, test for the presence of sulfide by placing a drop of sample on a lead acetate test strip that has been previously moistened with acetate buffer. If the test strip turns black, sulfide is present (above approximately 50 mg/L S^{2-}) and treatment is necessary as described below.

8.3.6.1 If the sample contains sulfide as indicated with a lead acetate test strip or is known to contain sulfides that will interfere with the test method, dilute the sample with reagent water until the lead acetate test strip no longer indicates the presence of sulfide (<50 mg/L S^{2-}) or until the interference is no longer significant to the analytical test method. For example, add 50 mL of freshly collected sample into a bottle containing 200 mL of reagent water, then test for sulfide again with the lead acetate test strip. If the test for sulfide is still positive, further dilution is required; however, be careful not to over dilute the sample as the detection limit will be elevated by this factor. In the aforementioned example, the dilution factor would be equal to 5 (total volume/sample volume). It is

TABLE 1 Examples of Potential Interferences if not Mitigated in Standard Cyanide Methods

Method	Description	Measurement	Interferences	Method Number
Total Cyanide	Automated UV	Colorimetric	Aldehydes Color Fatty Acids Mercury Nitrate Nitrite Oxidants Sulfides Turbidity Sulfur Compounds Thiocyanate	CFR Kelada-01, D4374
Total Cyanide	Manual Distillation with H_2SO_4 and $MgCl_2$	Amperometric	Aldehydes Carbonates Nitrite Nitrate Oxidants Sulfide Sulfur Compounds Thiocyanate	D7284, D2036 Test Method A
Total Cyanide	Manual Distillation with H_2SO_4 and $MgCl_2$	Manual or Automated Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Color Turbidity	D2036 Test Method A, EPA 335.2, EPA 335.4
Total Cyanide	Manual Distillation with H_2SO_4 and $MgCl_2$	ISE	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sulfide Sulfur Compounds Thiocyanate Color Turbidity	D2036 Test Method A, Standard Methods 4500-CN C/F
Total Cyanide	Manual Distillation with H_2SO_4 and $MgCl_2$	Titrimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D2036 Test Method A
Available Cyanide	Flow Injection Ligand Exchange	Amperometric	Carbonates Oxidants Sulfide	D6888, EPA OIA-1677
Cyanide Amenable to Chlorination	Alkaline Chlorination and Manual Distillations	Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sulfide Sulfur Compounds Thiocyanate Color Turbidity Unknowns that cause negative results	D2036 Test Method B

TABLE 1 *Continued*

Method	Description	Measurement	Interferences	Method Number
Weak Acid Dissociable Cyanide	Buffered Distillation	Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D2036 Test Method C
Weak Acid Dissociable Cyanide	Automated Method	Automated Colorimetric	Aldehydes Color Fatty Acids Mercury Nitrate Nitrite Oxidants Sulfides Turbidity	D4374
Weak Acid Dissociable Cyanide	Buffered Distillation	ISE	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D2036 Test Method C
Weak Acid Dissociable Cyanide	Buffered Distillation	Titrimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D2036 Test Method C
Weak Acid Dissociable Cyanide	Buffered Distillation	Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrite Nitrate Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Volatile Compounds	D2036 Test Method B
Metal Cyanide Complexes	Ion Chromatography	UV	Carbonate Dissolved Solids Metal Anions Metal Cations Oxidants Photodecomposition	D6994
Free Cyanide	Flow Injection	Amperometric	Carbonate Oxidants Sulfide	D7237
Free Cyanide	Microdiffusion	Colorimetric	Aldehydes Oxidants Sulfide Sulfur Compounds	D4282

TABLE 2 Potential Interferences with Selected Total Cyanide Methods Listed in 40 CFR Part 136

Methodology	Reference	Sample Processing	Determinative Step	Listed Interferences
Manual Distillation with Magnesium Chloride and Sulfuric Acid and Semi-Automated Colorimetry	EPA Method 335.4	The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution.	The cyanide ion in the absorbing solution is converted to CNCl by reaction with chloramine-T that subsequently reacts with pyridine and barbituric acid resulting in a red colored complex. The cyanide is determined with automated colorimetry.	(1) Oxidizing agents can destroy cyanides during storage. (2) Sulfide can complex with cyanide in sample or distillate. (3) Fatty acids cause interference during distillation. (4) Carbonate causes interference during distillation. (5) Aldehydes cause interference during distillation. (6) Glucose/Sugars cause interference during distillation. (7) Sulfur-containing compound causes interference during distillation by forming free sulfide that is captured in distillate. (8) Nitrate-Nitrite can cause high bias if sulfamic acid is not added during distillation
Manual Distillation with Magnesium Chloride and Sulfuric Acid	D2036 Test Method A	Total Cyanides is based on the decomposition of nearly all cyanides in the presence of strong acid, magnesium chloride catalyst, and heat during a 1-h reflux distillation.	Either the titration, colorimetric or selective ion electrode procedure can be used to quantify the cyanide concentration.	Common interferences in the analysis for cyanide include oxidizing agents, sulfides, aldehydes, glucose and other sugars, high concentration of carbonate, fatty acids, thiocyanate, and other sulfur containing compounds.
Manual Distillation with Magnesium Chloride and Sulfuric Acid	USGS I-3300-85	The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The distillation also removes certain interferences from water samples.	This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye.	Oxidizing agents may interfere. A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably. Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.
Cyanide by Automated Colorimetry	USGS I-4302-85	This method detects simple cyanides only; therefore, any complex cyanides must first be broken down by passing the acidified sample solution through an ultraviolet digestion-distillation procedure. The distillation step also removes certain interferences.	This method is based on the chlorination of cyanide with chloramine-T and on the subsequent reaction with a pyridine-barbituric acid reagent.	Oxidizing agents may interfere. A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably. Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.

recommended to perform this dilution during sample collection to avoid cyanide degradation; if this is not feasible, dilute the sample upon receipt in the laboratory and qualify the data. Clearly indicate the dilution volumes on the sample and chain-of-custody form so that the laboratory can mathematically correct the result.

8.3.6.2 Some analytical methods specify the use of lead carbonate or lead acetate to precipitate sulfide; however, sulfide and cyanide can form thiocyanate in the presence of lead sulfide causing decreased cyanide recoveries; therefore, lead carbonate and lead acetate should be avoided unless there is no other means to mitigate the sulfide or if the sample cannot be diluted as described in 8.3.6.1. Sulfide is removed by treating the sample with small increments of powdered lead carbonate or with the dropwise addition of lead acetate solution. Black lead sulfide precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with lead acetate test paper as indicated in 8.3.6. Immediately (within 15 minutes) filter with coarse filter paper (5 µm), then stabilize the sample according to 8.3.5. If the sample contains colloids that may contribute to the total cyanide concentration, filter the sample prior to adding the lead, then recombine the solids with the filtrate prior to analysis. Samples that are known or suspected to contain sulfides should be analyzed as soon as possible to avoid cyanide degradation.

TABLE 3 Interferences Introduced by Distillation

Compound	Description of Interference
Oxidizers	React with CN during distillation causing negative bias.
Sulfide	Distills over and can be detected as cyanide or it can form thiocyanate.
Oxidized Sulfur Compounds (except SO_4^{2-})	React with CN in absorber solution to form thiocyanate, cyanate, or both, causing negative bias.
Thiocyanate	Decomposes to oxidized sulfur compounds which react with cyanide in the absorber solution to form thiocyanate causing a negative bias.
Thiocyanate + Nitrate	Thiocyanate decomposes forming cyanide causing a positive bias.
Sulfur Dioxide	Sulfur Dioxide in the absorber solution can react with chloramine T during the colorimetric step resulting in a negative bias.
Nitrite + Organics	Can react to form Cyanide causing a positive bias.

TABLE 4 Possible Interferences for Determinative Step Used to Measure Cyanide

Technique	Interferences
Titration with Silver Ion	Sulfide, Phosphate, and Arsenate. Chloride if in excess.
Ion Selective Electrode	Sulfide, Silver, Bromide, Copper, Mercury, Lead, Thallium. Chloride if in excess.
Colorimetric	Thiocyanate, Sulfide, Cyanogen Chloride, reducing agents, color, dissolved solids, and turbidity.
Amperometry	>1500 mg/L Carbonate, Sulfide above 50 mg/L unless mitigated as described in D6888 – 04.

8.3.6.3 Precipitation of sulfide with cadmium chloride should be avoided since the formation of insoluble cadmium cyanide complexes can result in loss of cyanide. Sulfide volatilization techniques and methods that specify the addition of bismuth nitrate to treat sulfide during total cyanide distillations have been demonstrated by ASTM Subcommittee D19.06 to be ineffective.

8.3.6.4 Samples known or suspected to contain sulfide should be analyzed with an analytical test method that has been demonstrated to be free from sulfide interference. Test Method D6888 employs sulfide mitigation that can effectively remove up to 50 mg/L S^{2-} without prior treatment and has a lower method detection limit compared to colorimetric methods to compensate for any required dilutions specified in 8.3.6.1. To reduce or eliminate the need for dilution, samples containing up to 200 mg/L S^{2-} can be analyzed for available cyanide within 24 hours using Test Method D6888 if the sulfide abatement reagent is prepared with 4 g/L bismuth nitrate pentahydrate in 1 M H_2SO_4 instead of 1 g/L as described in the test method. Since sulfide competes with cyanide in the reaction with colorimetric methods, it is recommended to determine total cyanide with Test Methods D7284, D7511, or distill as described in Test Methods D2036 Test Method A or equivalent method (for example, MIDI distillation described in EPA Method 335.4) then analyze the distillate by Test Method D6888 with sulfide abatement. Alternatively, Test Methods D4374 specifies that up to 10 mg/L S^{2-} can be tolerated without significant interference. Samples and distillates known or suspected to contain sulfide should be processed as quickly as possible to avoid cyanide degradation.

8.3.7 *Sulfur*—To remove elemental sulfur (S_8), filter the sample immediately upon sample collection. If the filtration time will exceed 15 min, use a larger filter or a method that requires smaller sample volume. Syringe filters may be used for methods that do not require large sample volume. Do not use vacuum filtration as this may cause cyanide loss. If the sample contains a significant amount of particulate matter (for example, >1 % suspended solids) or if the sample is known or suspected to contain particulate cyanides (for example, ferric ferro cyanide or Prussian blue), save the solids for extraction as described in 8.4.3 on particulate cyanides, otherwise, discard the solids and filter.

8.3.8 *Aldehydes*—If formaldehyde, acetaldehyde, or other water-soluble aldehydes are known or suspected to be present, treat the sample with 2 mL 3.5 % ethylenediamine (6.10) per 100 mL of sample to avoid the formation of cyanohydrins. It has been found that this quantity of ethylenediamine addition is suitable to overcome the interference caused by up to 50 mg/L CH_2O present. Samples can be screened for the presence of formaldehyde and other water-soluble aldehydes using test strips for formaldehyde or aldehydes.

NOTE 2—Adding sodium hydroxide to pH 12 in samples containing formaldehyde, an ozone disinfection byproduct, can result in cyanide formation during sample storage.[7] Refer to 8.3.2 to determine the holding time.

8.3.9 *Chlorine, Hypochlorite, or other Oxidant*—Add a reducing agent only if an oxidant (for example, chlorine) is known or suspected to be present. Samples can be screened for oxidants by placing a drop of sample on a potassium-iodide

[7] Delaney, M. F., et al., "False Cyanide Formation during Drinking Water Sample Preservation and Storage," *Environmental Science and Technology*, Vol 41, No. 24, 2007, pp. 8383–8387.

(KI) starch paper. Reducing agents shown to be effective at removing oxidants are sodium thiosulfate ($Na_2S_2O_3$), ascorbic acid, sodium arsenite ($NaAsO_2$), or sodium borohydride ($NaBH_4$). However, some of these reagents have shown to produce a positive or negative cyanide bias, depending on other substances in the sample and the analytical method used. (**Warning—**When $NaBH_4$ is added to samples that contain arsenic, the formation of toxic arsine gas can occur. $NaBH_4$ can also produce hydrogen gas which could result in an explosion upon acidification of the sample.)

8.3.9.1 Unless the method specifies otherwise, sodium arsenite is the preferred reducing agent. Ascorbic acid can also be used; however, analysis must be performed within 24 hours to avoid cyanide degradation unless the holding time has been determined as described in Practice D4841 and 8.3.2. Methods recommending ascorbic acid specify adding 0.1 to 0.6 g/L. If $NaAsO_2$ is used, 100 mg/L $NaAsO_2$ will reduce more than 50 mg/L chlorine. After adding reducing agent, test the sample with a KI test strip to make sure all oxidant is removed. If oxidant remains, add more reducing agent, but avoid adding excess. Whatever agent is used, it should be tested to ensure that cyanide results are not affected adversely. Whenever a reducing agent is used to dechlorinate, nitrite could possibly form; therefore, sulfamic acid should be added during the distillation step for total cyanide determinations (for example, Test Methods D7284 and D2036 Test Method A) as described in 8.4.5.

8.3.10 After the sample has been treated for interferences that can be mitigated at the time of collection, refrigerate, then transport or ship to the laboratory. Refer to Guide D4840 for chain-of-custody procedures.

8.4 *Additional Laboratory Responsibilities:*

8.4.1 Upon receipt of sample(s) at the laboratory, verify that interferences are not present as indicated in this practice. At a minimum, test unknown samples for pH, sulfides and oxidants using pH indicator test strips, lead acetate test strips previously moistened with acetate buffer and KI starch paper, respectively. Document and mitigate any interference discovered in the laboratory, and if necessary, recollect the sample to mitigate the interference at time of collection. If resampling is not possible, qualify the result by describing the potential interference.

8.4.2 *Sulfite, Thiosulfate, or Thiocyanate*—Samples containing sulfite or thiosulfate can result in low cyanide recoveries when distilled followed by colorimetry as the determinative step. If thiocyanate is present, it can decompose into cyanide and sulfide during distillation or UV digestion, especially if oxidizing agents such as NO_3 are present. Colorimetric methods are susceptible to positive bias from thiocyanate even in the absence of oxidizers. If sulfite, thiosulfate, or thiocyanate are known or suspected to be present, use a method that has been demonstrated to be relatively free from these interferences.

8.4.2.1 For free or available cyanide, it is recommended to use gas diffusion separation with amperometric detection (for example, Test Methods D7237 and D6888).

8.4.2.2 For total cyanide, it is recommended to use a method with electrochemical or amperometric detection (for example, Test Methods D7284, D7511, or D2036 Test Method A using Test Method D6888 as the determinative step). Prior to distillation (Test Methods D7284, D2036), add 0.6 g/L ascorbic acid to the sample if it was not already added during sample collection; after adding ascorbic acid, the sample must be analyzed within 24 hours. Test the absorber solution as soon as possible after the distillation has completed.

NOTE 3—Adding sodium hydroxide to pH 12 in samples containing sulfite, a dechlorinating agent for wastewater treatment, can cause rapid cyanide degradation. Adding sodium hydroxide to samples containing thiocyanate in the presence of chloramines, which can be formed from the reactions of ammonia and chlorine, can result in cyanide formation during sample storage. Refer to 8.3.2 to determine the holding time.

8.4.3 *Particulate Cyanide*—If particulate cyanide is known or suspected to be present (for example, ferric ferrocyanide or Prussian blue) and total cyanide is required, stabilize the sample with NaOH during sample collection (8.3.5), then allow the sample to stand for at least 4 hours at room temperature prior to analysis in the laboratory. If the sample is known or suspected to contain particulate cyanide and will not be preserved with NaOH (8.3.5.1), or if the sample contains significant particulate content that will interfere with the test method (for example flow injection methods), filter 50.0 mL of solid containing sample with 5 µm filter paper and save the filtrate for analysis. Extract solids from this section or from 8.3.7 in 50 mL of 0.1 M NaOH solution by placing the filter paper in a vial and submersing the filter with 0.1 M NaOH solution for at least 4 hours. Decant or filter the extract prior to analysis. Alternatively, if a syringe type filter can be used to separate particulates, filter 10.0 mL of solid containing sample with 5 µm filter and desorb the solids captured on the filter by slowly passing 5 mL of 0.1M NaOH solution through the filter. Allow the wetted syringe filter to stand long enough to ensure that all cyanide complexes have been dissolved, then pass an additional 5 mL of 0.1 M NaOH solution through the filter. Do not use vacuum filtration as this may result in the loss of cyanide. Analyze total cyanide on the sample filtrate and solids extract separately. If cyanide is detected in the solids extract, colloidal cyanide is present and should be mathematically combined with the sample filtrate result.

8.4.4 *Carbonate*—Carbonate interference is evidenced by effervescence or foaming from the release of carbon dioxide upon acidification prior to distillation, which can cause a reduction in the pH of the absorber solution in Test Methods D2036 and D7284, resulting in low cyanide recovery. Carbonate above 1500 mg/L can cause negative bias or irregular peak shapes with gas diffusion amperometric methods such as Test Methods D6888 and D7511. If carbonate will interfere with the test method, adjust the pH to 12–12.5 prior to analysis with calcium hydroxide instead of adding sodium hydroxide in 8.3.5. It is preferable to add the calcium hydroxide at the time of sample collection instead of NaOH, but if the sample has already been submitted to the laboratory, add calcium hydroxide to pH 12–12.5 or until a precipitate forms. Allow the precipitate to settle then decant or filter the sample prior to analysis. However, if the sample contains insoluble complex cyanide compounds, they will not be included in the total cyanide determination. In this event, a measured amount of well-mixed treated sample can be filtered quantitatively with course filter paper (5 µm), but avoid vacuum filtration. The

filter is rinsed with dilute acetic acid (6.13) until the effervescence ceases, and the entire filter with the insoluble material is added to the filtrate. Alternatively, dilute samples in the laboratory prior to analysis to reduce interference from carbonate. Preserving samples with calcium hydroxide may decrease total cyanide recoveries; therefore, do not use calcium hydroxide unless the sample is known or suspected to contain carbonate at a concentration that is high enough to cause interference.

8.4.5 *Nitrate-Nitrite*—For total cyanide by Test Methods D2036, nitrite and nitrate in the sample can react under conditions of the distillation with other contaminants present to form cyanides. The addition of an excess of sulfamic acid to the sample prior to the addition of sulfuric acid will reduce this interference. For example, if samples are known or suspected to contain nitrate or nitrite, add 50 mL of 0.4N sulfamic acid solution (6.15) per 500 mL sample, then proceed with distillation after 3 minutes. For MicroDist, follow directions in Test Method D7284 for adding sulfamic acid prior to distillation. Do not add excessive sulfamic acid as this could create method bias.

8.4.6 *Quality Control and Reporting Requirements*—Report cyanide as CN^- (usually in µg/L) and correct for any dilutions that may be done in the field or laboratory. Indicate the type of cyanide (for example, free, available, or total) and standard method used to make the determination. Make note of any specific mitigation of interference that was performed in the laboratory; if interference removal or suppression is not documented in this practice, provide a reference or supporting data to justify the action. In addition to the quality control requirements specified in the analytical method, it is recommended to perform a laboratory matrix spike and matrix spike duplicate to evaluate precision and recovery for unknown matrices; although acceptable recoveries do not necessarily rule out the possibility of interference. For further information evaluating matrix spike duplicates, see Practice D5847. If interference is still suspected, sample characterization may be necessary to identify and mitigate the potential interference(s).

9. Keywords

9.1 available cyanide; cyanide; free cyanide; hydrogen cyanide; interference; preservative; sample collection; total cyanide

APPENDIX

(Nonmandatory Information)

X1. EXAMPLES OF HOLDING TIME STUDIES

X1.1 A synthetic cyanide challenge matrix (X1.1.1) was prepared and tested with Test Method D6888 – 04 periodically for 14 days to estimate the holding time as described in Practice D4841. As shown in Table X1.1 and Fig. X1.1, the holding time is approximately 7 days.

X1.1.1 *Cyanide Challenge Matrix Solution*—Prepare a stock solution by transferring 0.954 g NH_4Cl, 1.80 g KNO_3, 7.03 g Na_2SO_4, 0.483 g KOCN, and 0.251 g KSCN into a 1L volumetric flask containing 100 mL of water, then dilute to volume with water. The challenge matrix solution is then made

TABLE X1.1 Holding Time Evaluation without NaOH Preservation

Sample Description	Synthetic Challenge Matrix Sample (No NaOH)			Fortified CN^-, ug/L		200	
	Available Cyanide, µg/L						
Holding Time, Days	0	1	2	6	7	9	14
Replicate 1	201	213	204	218	196	196	191
Replicate 2	207	211	207	215	194	200	194
Replicate 3	214	212	204	210	205	201	195
Replicate 4	216						
Replicate 5	215						
Replicate 6	204						
Replicate 7	212						
Replicate 8	216						
Replicate 9	217						
Replicate 10	215						
Average	212	212	205	214	198	199	193
Standard Deviation	5.66	1.00	1.73	4.04	5.86	2.65	2.08
%RSD	2.67	0.47	.085	1.92	2.86	1.32	1.07
Tolerable Range of Variation from Initial Mean (±)			99% Confidence Interval				
10.62	222		Upper Control Limit				
	201		Lower Control Limit				

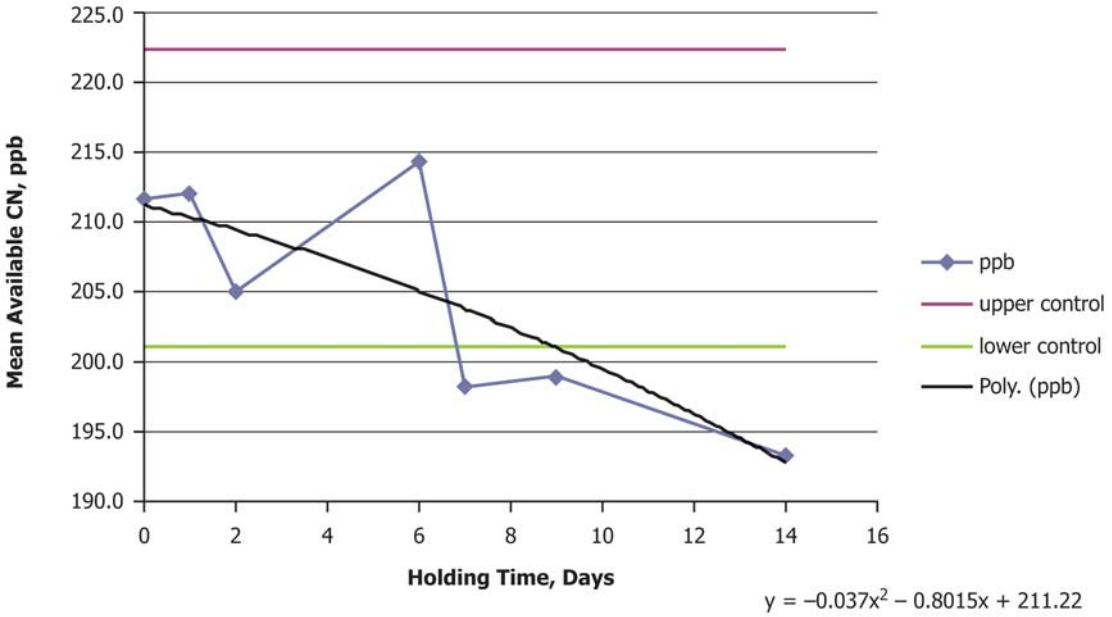

FIG. X1.1 Holding Time Evaluation of Challenge Matrix without NaOH Preservation, Available Cyanide Test Method D6888

by diluting the stock solution by a factor of 10 (for example, 100 mL stock solution plus 900 mL water). This solution can be used as a reproducible matrix for quality control samples and to verify performance of cyanide methods. The challenge matrix solution contains 25 mg/L NH_3 as N, 25 mg/L NO_3 as N, 475 mg/L SO_4, 25 mg/L OCN and 15 mg/L SCN. Additional interferences can be added for evaluation as necessary. The challenge matrix was not preserved in this example; to preserve add NaOH to pH 10–11 after preparation.

X1.2 Similarly, a public utility agency effluent sample was fortified with 10 µg/L free cyanide, and the samples were tested for aquatic free cyanide with Test Method D7237 – 06 during a 6 day period. The estimated holding time in the unpreserved effluent sample was determined to be greater than 6 days with Practice D4841 since all of the samples were within the control limits during the timeframe of the study. In this case, the samples are always tested within 48 hours; therefore, the length of the holding time was not extended. A summary of the data are shown in Table X1.2 and Fig. X1.2.

TABLE X1.2 Practice D4841 Laboratory Estimation of Holding Time for Aquatic Free Cyanide Test Method D7237 – 06, Preservation <6°C, no NaOH

Utilities Agency Effluent, Fortified with 10 ppb Free Cyanide									
					Aquatic Free Cyanide, µg/L				
	Initial	18.25 hours	19.75 hours	23 hours	45.5 hours	50 hours	69 hours	74 hours	143 hours
Replicate 1	11.0	9.8	9.9	9.8	9.7	9.9	10.2	10.1	9.4
Replicate 2	10.5								
Replicate 3	10.3								
Replicate 4	10.3								
Replicate 5	9.7								
Replicate 6	10.8								
Replicate 7	10.3								
Replicate 8	11.0								
Replicate 9	10.5								
Replicate 10	10.7								
Average	**10.5**	9.8	**9.9**	**9.8**	**9.7**	**9.9**	**10.2**	**10.1**	**9.4**
Standard Deviation	**0.89**								
% RSD	**3.71**								
Tolerable Range of Variation from Initial Mean (*)		99 % Confidence Interval							
1.27		11.79		Upper Control Limit					
		9.25		Lower Control Limit					

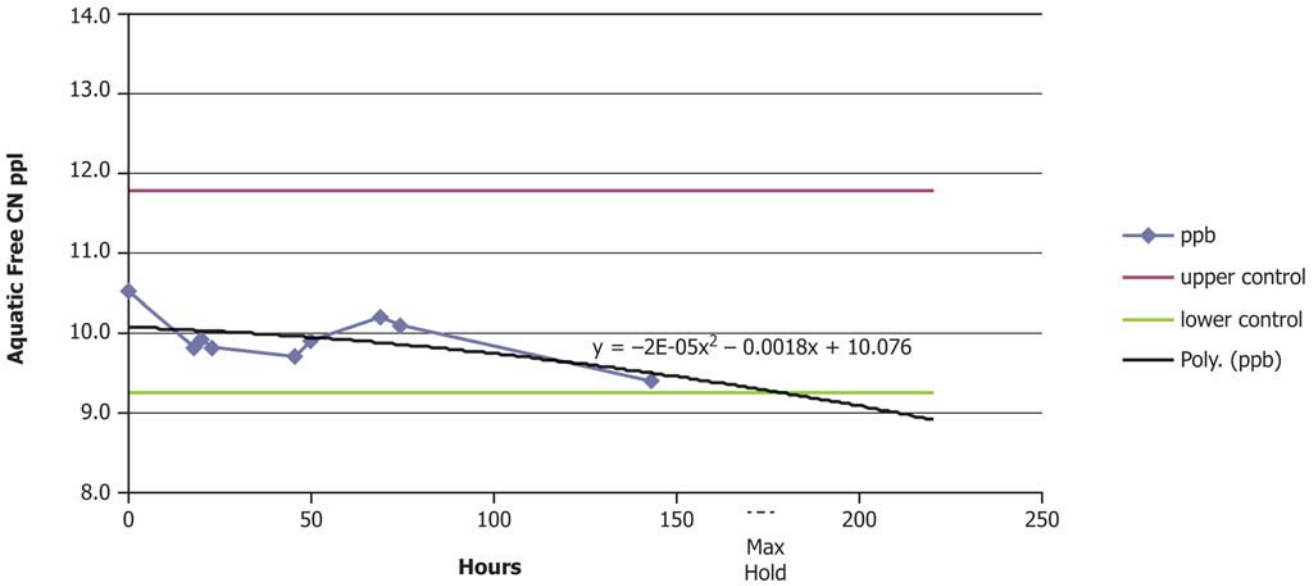

FIG. X1.2 Estimation of Holding Time of Utilities Agency Effluent Sample, Aquatic Free Cyanide Test Method D7237